

10/664,883

REMARKS

This Amendment is being filed in response to the final Office Action dated November 23, 2007. In view of these amendments and remarks this amendment should be entered, the application allowed, and the case passed to issue. No new matter or considerations are introduced by this amendment. Claim 8 is amended to correct the informality noted by the Examiner. Support for the amendment to claim 8 is found in claim 1. Even if this application is not allowed, the amendment should still be entered upon the filing of an appeal as the amendment significantly reduces the issues for appeal.

Claims 1-8 and 10-19 are pending this application. Claims 1-8 and 10-19 are rejected. Claim 8 has been amended in this response. Claim 9 was previously canceled.

Claim Rejections Under 35 U.S.C. § 112

Claim 8 was rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for insufficient antecedent basis. This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

Claim 8 has been amended to correct the asserted informalities. Applicants submit that the claims fully comport with the requirements of 35 U.S.C. § 112.

Claim Rejections Under 35 U.S.C. § 103

Claims 1, 5, 6, 11, 13, and 15 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Barlow et al. (US 5,411,818) in view of Yamamoto et al. (U.S. 2003/0129495). This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested. The following is a comparison between the invention, as claimed, and the cited prior art.

An aspect of the invention, per claim 1, is a stacked battery (30) comprising an electrode stacked body (7) formed by stacking a sheet electrode (10) and an electrolyte layer (4). The

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electrode (10) includes a single-layered collector (1). The electrolyte layer (4) is placed between the electrodes (10). The collector (1) has an approximately rectangular shape in a plane perpendicular to the stacking direction. A packaging material (5a, 5b) houses the electrode stacked body (7). The packaging material (5a, 5b) has an opening which faces the stacking direction of the electrode stacked body (7). The electrodes (10) are placed on outermost layers of the electrode stacked body (7) in such a manner so that the single-layered collectors (1a, 1b) are exposed through the opening to an outside of the stacked battery (30) in the stacking direction of the electrode stacked body (7) and function as terminals. A center of the surface of the collector, is a surface perpendicular to the stacking direction of the electrode stacked body, is exposed through the opening to the outside of the stacked battery.

The combination of Barlow et al. and Yamamoto et al. do not suggest a stacked battery wherein the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that the single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, and wherein a center of a surface of the collector, which is a surface perpendicular to the stacking direction of the electrode stacked body, is exposed through the opening to the outside of the stacked battery, as required by claim 1; and wherein the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that outermost single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, as required by claim 13.

The Examiner asserted that Barlow et al. disclose in Fig. 2B disclose a stacked battery wherein the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that the single-layered collectors are exposed through the opening to an outside of the

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stacked battery in the stacking direction of the electrode stacked body and function as terminals, wherein the packaging material and the outermost collectors together form a housing and the collectors form substantial portion of the housing. The Examiner relied on Yamamoto et al. for teaching that secondary batteries may be any number of shapes.

The Examiner interpreted seals 22, 24 of Barlow et al.'s battery as the packaging material according to the present claims. The seals 22, 24, however, function as members that prevent the migration of electrolyte around the bipolar walls, and thus prevent the formation of ionically conducting paths (column 1, lines 7-12 and column 2, lines 27-30). Barlow et al. is directed to high temperature lithium alloy/metal sulfide batteries with molten salt electrolytes (column 3, lines 21 to 26). Though it is not shown in the Figures of Barlow et al., the Barlow et al. battery must have an outer case. It would be impractical to use the Barlow et al. battery without an outer case. It needs the outer case for both structural integrity and insulation (see Linden et al., *Handbook of Batteries*, 3d Ed., pp. 21.3-21.9 and 41.1 to 41.6 and 41.20 to 41.22).

High temperature molten alkali halide salt batteries, such as LiCl-KCl eutectic electrolyte batteries, have an operating temperature of at least 400 °C (Linden et al. at 41.1). Therefore, the battery of Barlow et al. would require an outer case and insulation to prevent electrolyte freezing and battery shutdown (Linden et al. at 21.6 to 21.7). The requirement that the battery operating temperature of liquid (molten) alkali halide salt electrolyte batteries be maintained above the melting point of the electrolyte salt is clearly well known in the art, as evidenced by Linden et al.

Furthermore, Barlow teaches that the battery stack is not hermetically sealed (column 2, lines 27-30). One of skill in this art recognizes that lithium alloy batteries are hygroscopic and the absorption of water severely impacts the performance of lithium alloy batteries. Therefore, hermetic sealing is critical in a lithium alloy battery. Thus, it would be immediately clear to one

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ordinary skill in this art that an outer battery casing would be required in the battery of Barlow et al. to provide a hermetic seal.

Because the battery of Barlow et al. requires an outer case, Barlow et al. does not disclose or suggest that the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that the single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, and wherein a center of a surface of the collector, which is a surface perpendicular to the stacking direction of the electrode stacked body, is exposed through the opening to the outside of the stacked battery, as required by claim 1; and wherein the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that outermost single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, as required by claim 13.

Yamamoto et al. do not cure the deficiencies of Barlow et al.

Claims 2, 3, and 14 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Barlow et al. in view of Yamamoto et al. and further in view of Williams et al. (US 5,254,415). This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

The Examiner acknowledged that Barlow et al. and Yamamoto et al. do not disclose hermetic sealing. The Examiner relied on the teaching of Williams et al. that hermetically sealing the battery would prevent electrolyte from leaking out.

The combination of Williams et al. with Barlow et al. and Yamamoto et al., however, do not suggest the claimed stacked battery. As explained above, Barlow et al. expressly teach that the stack illustrated in Fig. 2B is not hermetically sealed. Hermetically sealing the stack of Barlow et al. would require an outer battery case, and as explained above when the outer case is

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included with the stack of Barlow et al., the electrodes can not be placed on outermost layers of the electrode stacked body in such a manner so that the single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, and wherein a center of a surface of the collector, which is a surface perpendicular to the stacking direction of the electrode stacked body, is exposed through the opening to the outside of the stacked battery, as required by claim 1; and the electrodes can not be placed on outermost layers of the electrode stacked body in such a manner so that outermost single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, as required by claim 13.

Furthermore, as illustrated in Fig. 1, Williams et al. disclose that positive and negative terminals (16, 18) are exposed through an opening to an outside of a stacked cell array (12) in the stacking direction of the stacked cell array (12), but fail to disclose current collectors (30A, 32N) are exposed through the opening to the outside of the stack cell array (12). The positive terminal (16) and the current collector (30A) (and negative terminal (18) and current collector (32N) are placed on an outermost of the cell stack array (12). Thus, an electric current flows through the positive terminal (16) and the current collector (30A), thereby the output power is reduced due to an increase in the electrical resistance between the positive terminal (16) and the current collector (30A).

In the present invention, however, the outermost current collectors (1a, 1b) are single-layered, therefore increased electrical resistance, such as in the Williams et al. battery, is not created.

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Claims 8, 12, and 17 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Barlow et al. in view of Yamamoto et al. and further in view of Arias (US 5,618,641). This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

The combination of Barlow et al., Yamamoto et al., and Arias do not suggest the claimed stacked battery because Arias does not cure the deficiencies of Barlow et al. and Yamamoto et al. Arias does not suggest that the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that the single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, and wherein a center of a surface of the collector, which is a surface perpendicular to the stacking direction of the electrode stacked body, is exposed through the opening to the outside of the stacked battery, as required by claim 1; and wherein the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that outermost single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, as required by claim 13.

Claims 18 and 19 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Barlow et al. in view of Yamamoto et al. and further in view of Murata (US 5,378,557). This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

The combination of Barlow et al., Yamamoto et al., and Murata do not suggest the claimed stacked battery because Murata does not cure the deficiencies of Barlow et al. and Yamamoto et al. Murata does not suggest that the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that the single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, and wherein a center of a surface of the collector, which

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is a surface perpendicular to the stacking direction of the electrode stacked body, is exposed through the opening to the outside of the stacked battery, as required by claim 1; and wherein the electrodes are placed on outermost layers of the electrode stacked body in such a manner so that outermost single-layered collectors are exposed through the opening to an outside of the stacked battery in the stacking direction of the electrode stacked body and function as terminals, as required by claim 13.

The dependent claims are allowable for at least the same reasons as the respective independent claims from which they depend and further distinguish the claimed stacked battery.

In view of the above amendments and remarks, Applicants submit that this amendment should be entered, the application allowed, and the case passed to issue. If there are any questions regarding this Amendment or the application in general, a telephone call to the undersigned would be appreciated to expedite the prosecution of the application.

To the extent necessary, a petition for an extension of time under 37 C.F.R. 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

McDERMOTT WILL & EMERY LLP

Bernard P. Codd

Bernard P. Codd

Registration No 46,429

600 13th Street, N.W.
Washington, DC 20005-3096
Phone: 202.756.8000 BPC:MWE
Facsimile: 202.756.8087
Date: February 13, 2008

**Please recognize our Customer No. 20277
as our correspondence address.**

HANDBOOK OF BATTERIES

David Linden Editor

Thomas B. Reddy Editor

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ability and long shelf life. Consequently, they have been used in space exploration. Figure 21.1 illustrates typical

The disadvantages of thermal batteries include:

1. Generally short activated lives (typically less than 10 min), but they can be designed to operate for more than 2 hours.
2. Low to moderate energy densities and specific energies.
3. Surface temperatures can typically reach 230°C or higher.
4. Voltage output is nonlinear, and decreases with life.
5. One time use. Once activated, they cannot be turned off or reused (recharged).

21.2 DESCRIPTION OF ELECTROCHEMICAL SYSTEMS

A number of electrochemical systems have been used in thermal batteries. As materials and techniques have improved the state-of-the-art (SOA) performance of these batteries, older designs have gradually disappeared. Battery designs with older technologies still exist, however, and continue to be manufactured. In some cases, the continuing production of an "antiquated" system is driven by economics. Redesign and requalification of an existing battery with a newer technology is often economically unacceptable. Table 21.1 lists some of the more common types of electrochemical systems that have been used over the years.

All thermal battery cells consist of an alkali or alkaline earth metal anode, a fusible salt electrolyte, and a metal salt cathode. The pyrotechnic heat source is usually inserted between cells in a series cell-stack configuration.

TABLE 21.1 Types of Thermal Batteries

Electrochemical system: anode/electrolyte/cathode	Operating cell voltage	Characteristics and/or applications
LiCl-KCl/K ₂ Cr ₂ O ₇	2.8-3.3	Very fast activation times; short lives; used in "pulse" applications
LiCl-KCl/WO ₃	2.4-2.6	Medium-short lives; low electrical noise; not severe physical environments
LiCl-KCl/CuCrO ₂	2.2-2.6	Medium lives; severe dynamic environments
LiCl-KCl/V ₂ O ₅	2.2-2.7	Medium-short lives; severe physical environments
LiCl-KCl/PbCrO ₄	2.0-2.7	Fast activation; short lives
LiBr-KBr/K ₂ Cr ₂ O ₇	2.0-2.5	Short lives; used in high-voltage, low-current applications
LiCl/LiCl-LiBr-LiF/FeS ₂	1.6-2.1	Short to medium lives, high current capacity; severe physical environments
LiCl/LiCl-KCl/FeS ₂	1.6-2.2	Long lives, high current capacity; severe physical environments
LiCl/LiBr-KBr-LiF/CoS ₂	1.6-2.1	Long lives (past 1 h), high current capacity; severe physical environments

21.4 CHAPTER TWENTY-ONE

21.2.1 Anode Materials

Until the 1980s, most thermal battery designs employed a calcium metal anode—with calcium foil generally attached to an iron, stainless steel, or nickel foil current collector or backing. A "bimetal" anode is manufactured by vapor depositing the calcium on the backing material. Here, the calcium anode thickness usually ranges between 0.03 and 0.25 mm. In other designs, calcium foil is either pressed onto a perforated "cheese grater"-type backing sheet, or is spot-welded to the backing. Magnesium metal is another anode material that has been widely used, both in "bimetal"-form and in pressed or spot-welded anode configurations.

Introduced in the mid-1970s, lithium has become the most widely used anode material in thermal batteries. There are two major configurations of lithium anodes: lithium alloy and lithium metal. The most commonly used alloys are lithium aluminum, with about 20 weight percent lithium and lithium (silicon), with about 44 weight percent lithium. Lithium-boron alloy has also been evaluated, but has not been used widely because of its higher cost.

LiAl and Li(Si) alloys are processed into powders, which are cold-pressed into anode wafers or pellets that range in thickness from 0.75 to 2.0 mm. In the cell, the alloy pellet is backed with an iron, stainless steel, or nickel current collector. Lithium alloy anodes function in activated cells as solid anodes, and must be maintained below melt or partial melt temperatures. Forty-four weight percent Li(Si) alloy will partially melt at 709°C, while α , β -LiAl will exhibit partial melting at 600°C. If these melting temperatures are exceeded, the melted anode may come in contact with cathode material, allowing a direct, highly exothermic chemical reaction and cell short-circuiting.

Lithium metal anodes function in activated cells at temperatures above the melting temperature of lithium, 181°C. To prevent the molten lithium from flowing out of the cells and short-circuiting the battery, it is combined with a high-surface-area binder of metal powder or metal foam. The binder holds the lithium in place by surface tension.

Lithium metal anodes are prepared by combining the binder material with molten lithium, followed by pressing the solidified mixture into thin foil, typically 0.07 to 0.65 mm thick. The foil is then cut into cell-sized parts. The anode foil parts are enclosed in iron-foil caps, which provide added protection against the migration of any free lithium (which can result in cell shorting) and also serve as electron collectors (electrical connections). Such anodes can function at cell temperatures greater than 700°C without significant loss of performance.⁵ Each thermal battery designer or manufacturer has developed a number of anode configurations, from which the most suitable may be selected, depending upon specific battery performance requirements.

21.2.2 Electrolytes

Historically, most thermal battery designs have used a molten eutectic mixture of lithium chloride and potassium chloride as the electrolyte (45:55 LiCl:KCl by weight, mp = 352°C). Halide mixtures containing lithium have been preferred because of their high conductivities and general overall compatibility with the anodes and cathodes. Compared to most lower-melting oxygen-containing salts, the halide mixtures are less susceptible to gas generation via thermal decomposition or other side reactions. More recent electrolyte variations, containing bromides, have been developed for thermal batteries to achieve a lower melting point (and thus extend the operating life) or to reduce the internal resistance (and raise the current capability) of the batteries. These include LiBr-KBr-LiF (mp = 320°C), LiCl-LiBr-KBr (mp = 321°C), and the all-Li⁺ electrolyte LiCl-LiBr-LiF (mp = 430°C).⁶ Electrolytes with mixtures (e.g., Li⁺ and K⁺, instead of all-Li⁺) are subject to the establishment of Li⁺ concentration gradients during discharge. These concentration gradients can give rise to localized

At battery operating temperatures, the viscosity of molten salt electrolytes is very low (ca. 1 centipoise). In order to immobilize the molten electrolytes, binders are added to the salts during compounding. Earlier blends, originally developed for Ca/CaCrO₄ systems and the original LiAl/FeS₂ batteries, employed clays, such as kaolin, and fumed silica as effective binders for the salts. These siliceous materials will react with Li(Si) and lithium metal anodes, however. High surface area MgO is sufficiently inert for the more reactive anodes, and is presently the binder of choice in most systems.

Cathode Materials

A wide variety of cathode materials has been used for thermal batteries. These include calcium chromate (CaCrO₄), potassium dichromate (K₂Cr₂O₇), potassium chromate (K₂CrO₄), lead chromate (PbCrO₄), metal oxides (V₂O₅, WO₃), and sulfides (CuS, FeS₂, CoS₂). The criteria for suitable cathodes include high voltage against a suitable anode, compatibility with halide melts, and thermal stability to approximately 600°C. Calcium chromate has been most often used with calcium anodes because of its high potential (at 500°C, $V = 2.7$) and its thermal stability at 600°C. FeS₂ and (more recently) CoS₂ are used with modern lithium-containing anodes (FeS₂ to 550°C and CoS₂ to 650°C).

2.4 Pyrotechnic Heat Sources

The two principal heat sources that have been used in thermal batteries are heat paper and heat pellets. Heat paper is a paper-like composition of zirconium and barium chromate powders supported in an inorganic fiber mat. Heat pellets are pressed tablets or pellets consisting of a mixture of iron powder and potassium perchlorate.

The Zr-BaCrO₄ heat paper is manufactured from pyrotechnic-grade zirconium powder and BaCrO₄, both with particle sizes below 10 microns. Inorganic fibers, such as ceramic and glass fibers, are used as a structure for the mat.⁶ The mix, together with water, is formed into a paper—either as individual sheets by use of a mold or continuously through a paper-making process. The resultant sheets are cut into parts and dried. Once dried, the material must be handled very carefully since it is very susceptible to ignition by static charge and friction. Heat paper has a burning rate of 10 to 300 cm/s and a usual heat content of about 1675 J/g (400 cal/g). Heat paper combusts to an inorganic ash with electrical resistivity. If inserted between cells, it must be used in combination with highly conductive inter-cell connectors. In some battery designs, combusted heat paper serves as an electrical insulator between cells. In those applications it may have an additional layer of ceramic fibers only, known as *base sheet*, to enhance its dielectric properties. In most modern pellet-type batteries, heat paper is used only as an ignition or fuse train, if at all. In this application, the heat paper fuse, which is ignited by the initiator, in turn ignites the heat pellets, which are the primary heat source in these batteries.

Heat pellets are manufactured by cold-pressing a dry blend of fine iron powder (1 to 10 micron) and potassium perchlorate. The iron content ranges from 80 to 88% by weight, and is considerably in excess of stoichiometry. Excess iron provides the combusted pellet with sufficient electronic conductivity, eliminating the need for separate inter-cell connectors. The heat content of Fe-KClO₄ pellets ranges from 920 J/g for 88% iron to 1420 J/g for 80% iron. Burning rates are generally slower than those of heat paper, and the energy required to ignite them is greater. For that reason, the heat pellet is less susceptible to inadvertent ignition during battery manufacture. Heat pellets (and especially unpelletized heat powder) must, nevertheless, be handled with extreme care and protected from potential ignition sources.

After combustion, the heat pellet is an electronic conductor, simplifying inter-cell connection and battery design. It also retains its physical shape and is very stable under dynamic environments (such as shock vibration and spin). This contributes greatly to the general ruggedness of battery designs that incorporate heat pellets. Another major advantage of heat pellets is that their enthalpy of reaction is much higher than that of heat paper ash. Thus, they serve as heat reservoirs, retaining considerable heat after combustion, and tend to extend the battery active life by virtue of their greater thermal mass.

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21.6 CHAPTER TWENTY-ONE**21.2.5 Methods of Activation**

Thermal batteries are activated by applying an external signal to an initiation device that is incorporated in the battery. There are four generally used methods of activation: electric signal to an electric igniter; mechanical impulse to a percussion primer; mechanical shock to an inertial activator; and optical energy (laser) signal to a pyrotechnic material.

Electric igniters typically contain one or more bridge wires and a heat-sensitive pyrotechnic material. Upon application of an electric current, the bridge wire ignites the pyrotechnic, which in turn ignites the heat source in the thermal battery. Igniters generally fall into two categories: squibs and electric matches. A typical squib is enclosed in a sealed metal or ceramic enclosure and contains one or two bridge wires. The most commonly used types require a minimum activation current of 3.5 A and have a maximum no-fire limit of 1 A or 1 W (whichever is greater). Electric matches do not have a sealed enclosure and typically contain only one bridge wire. They require an activation current of 500 mA to 5 A and should not be subjected to a no-fire test current of more than 20 mA. Squibs are 4 to 10 times more expensive than electric matches, but are required for applications that may encounter environments with electromagnetic radiation.

Percussion primers are pyrotechnic devices that are activated by impact from a mechanical striking device. Typically, a primer is activated by an impact of 2016 to 2880 g·cm applied with a 0.6 to 1.1 mm spherical radius firing pin. Primers are installed in primer holders that are integral parts of the battery enclosure.

Inertial or setback activators are devices that are activated by a large-magnitude shock or rapid acceleration, as is generated upon firing of a mortar or artillery round. They are designed to react to a predetermined combination of g force and its duration. Inertial activators are typically firmly mounted inside the battery structure in order to withstand severe dynamic environments.

Optical energy (laser) activation of thermal batteries is accomplished by "firing" a laser beam through an optical "window" installed in the outer enclosure of the battery and igniting a suitable pyrotechnic material inside the unit. This method has found utility in applications where severe electromagnetic interference would be disruptive to an electrical firing method.

Thermal batteries can be equipped with more than one activation device. The multiple activators can be of the same type or of any combination required by the application.

21.2.6 Insulation Materials

Thermal batteries are designed to maintain hermeticity throughout their service lives, even though their internal temperatures reach or even exceed 600°C. The thermal insulation used to retard heat loss from the cell stack and minimize peak surface temperatures must be anhydrous and must have high thermal stability. Ceramic fibers, glass fibers, certain high-temperature polymers, and their combinations have been used as thermal insulators. Older battery designs may still have asbestos insulation, which was widely used before the 1980s.

Electrical insulation materials for conductors, terminals, initiators, and other electrically conductive components are typically made of mica, glass or ceramic fiber cloths, and high temperature-resistant polymers.

Thermal insulation is located around the periphery and at both ends of the cell stack. Some designs also incorporate high-temperature epoxy potting materials as insulation and structural support for the initiators and electric conductors on the terminal end (header) of the batteries. Long-life batteries (20+ min.) usually incorporate high-efficiency thermal insulation materials such as Min-K (Johns Manville Co.) or Micro-Therm (Constantine Wingate, Ltd.). Extended life batteries (1 hr and longer) may incorporate vacuum blankets and/or double cases with vacuum space between them to retard heat loss. Special high-thermal-capacity pellets and extra "dummy" cells are also used at the ends of cell stacks to retard heat loss and thus prolong the activated life of some batteries.⁹ Figure 21.2 shows a typical arrangement of thermal insulation and an encapsulated header assembly with initiator (squib).

21.3 CEL

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9 Figure 21.2 shows a typical
assembly with initiator (squib)

THERMAL BATTERIES 21.7

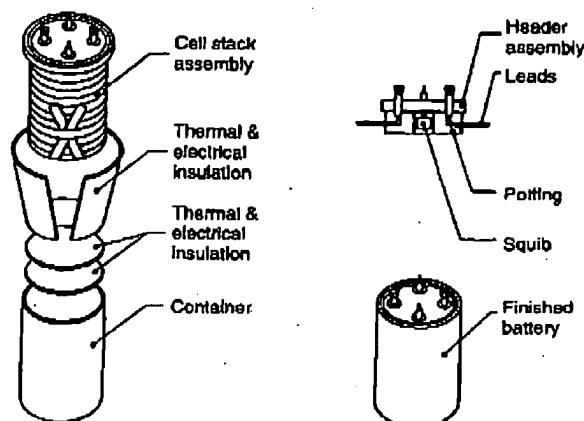


FIGURE 21.2 Typical thermal battery assembly. (Courtesy of Eagle-Picher Technologies, LLC.)

A very effective method for extending the activated battery life and reducing the effects of heat on thermally sensitive components located near the battery is to use an external thermal blanket. Provided that it is protected from external contamination, a thermal blanket is more effective than internal insulation, primarily because the hot gasses that are generated inside the battery during activation cannot penetrate it. External insulation, mounting methods, and the surrounding environment have a significant effect on the heat loss from the battery and all of these must be taken into consideration in the design of thermal batteries.

21.3 CELL CHEMISTRY

A wide variety of different cell chemistries have been developed and used in thermal batteries. At this time, the most widely used chemistry is lithium/iron disulfide (Li/FeS_2), with calcium/calcium chromate (Ca/CaCrO_4) as a distant second. There are special applications, though, where one of the other less used chemistries could offer special advantages. As an example, the requirement for a very fast activation time with a relatively short activated life would be provided by the calcium/potassium dichromate ($\text{Ca}/\text{LiCl-KCl}/\text{K}_2\text{Cr}_2\text{O}_7$) system or the calcium/lead chromate ($\text{Ca}/\text{LiCl-KCl}/\text{PbCrO}_4$) system. For a very general overview, Table 21.2 lists some example-specific performance characteristics of various thermal battery chemistries and designs.

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TABLE 21.2 Characteristics of Various Thermal Batteries

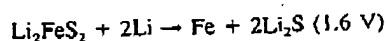
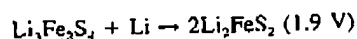
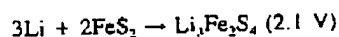
Cell type	Volume, cm ³	Weight, g	Nominal voltage, V	Current, A	Peak power, W	Average life, s	Specific energy (Wh/kg)	Energy density (Wh/L)
Cup/WO ₃	450	850	7	5.8	41	70	2.3	4.3
Open cell/tape/WO ₃	100	385	50	0.36	15	70	1.3	50.2
Open cell/tape/dichromate	44	148	18	26.0	462	1.2	1.0	3.5
Open cell/tape/dichromate	1	5.5	10	5.0	50	0.15	0.4	2.1
Open cell/tape/bromide	81	225	203	0.02	4	45	0.2	0.7
Pellet/CaCrO ₄ /heat paper	123	310	42	2.9	125	25	2.8	6.8
Pellet/CaCrO ₄ /heat pellet	105	307	28	1.2	34	150	4.6	13.4
Pellet/CaCrO ₄ /heat pellet	105	307	28	2.5	75	60	3.8	11.1
Pellet/LiM*/FeS ₂	92.3	320	25	15.0	420	35	11.4	39.0
Pellet/LiM*/FeS ₂	170	505	28	12.0	378	140	26.2	82.0
Pellet/LiM*/FeS ₂	208	544	138	1.0	138	250	32.2	84.1
Pellet/LiM*/FeS ₂	3120	6620	315	10.0	3600	250	33.1	77.0
Pellet/LiM*/FeS ₂	334	907	65	7.95	541	320	43.0	116.0
Pellet/LiM*/FeS ₂	552	1400	27	12.0	372	600	38.7	111.8
Pellet/LiM*/FeS ₂	1177	270	27	17.0	459	900	35.1	97.5

M*—either alloy or metal.

21.3.1 Lithium/Iron Disulfide

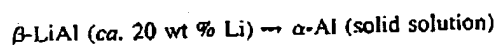
There are three common lithium anode configurations: Li(Si) alloy, LiAl alloy, and Li metal in metal matrix, Li(M), where the matrix is usually iron powder. With the difference that the alloy anodes remain solids and the lithium in the Li(Fe) mix is molten in an activated cell, all three anodes participate in the cell reaction similarly. All may be used with the same FeS₂ cathode and the same electrolytes. These electrolytes may be the basic LiCl-KCl eutectic electrolyte, LiCl-LiBr-LiF electrolyte for best ionic conductivity, or a lower-melting point electrolyte such as LiBr-KBr-LiF for extended activated life. Since the FeS₂ is a good electronic conductor, the electrolyte layer is necessary in order to prevent direct anode-cathode contact and cell short-circuiting. When molten, the electrolyte between the anode and the cathode is held in place by capillary action through the use of a chemically compatible (inert) binder material. MgO is the preferred material for this application.¹⁰

The Li/FeS₂ electrochemical system has become the preferred system because it does not contain any parasitic chemical reactions. The extent of self-discharge depends on the type of electrolyte used and the cell temperature.¹¹ The predominant discharge path for cathode is:



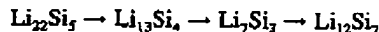
Most batteries are designed to use only the first and sometimes the second cathode transition to avoid changes in cell voltage.

The transitions that occur at the anode depend on the alloy used. For LiAl:



Below approximately 18.4 weight percent lithium (lower limit for all β -LiAl) and above 10 weight percent lithium (upper limit for α -Al), the alloy is two-phase α, β -LiAl. This fixes the alloy voltage on a plateau. This plateau is about 300 mV less than the voltage afforded by pure lithium metal.

The composition transitions for Li(Si) are:



An anode voltage plateau is defined for compositions falling between each adjacent pair of alloys. That is, the first plateau occurs between $\text{Li}_{22}\text{Si}_5$ and $\text{Li}_{13}\text{Si}_4$. The 44 weight percent Li(Si) composition falls here, and begins its discharge approximately 150 mV less than that of pure lithium.

The use of FeS_2 as a cathode material can cause a large voltage transient or "spike" of 0.2 V or more per cell, which is evident immediately after activation and lasts from milliseconds to a few seconds. This phenomenon is related to the impact of temperature, the amounts of electroactive impurities in the raw material (iron oxides and sulfates), elemental sulfur from FeS_2 decomposition, and the activity of lithium not being fixed in the cathode. In applications where the voltage has to be well regulated, this "spike" is not acceptable. The voltage transient can be virtually eliminated by the addition of small amounts of Li_2O or Li_2S (typically 0.16 mol Li per mol FeS_2) to the catholyte (FeS_2 and electrolyte blend), a method known as *multiphase lithiation*.¹² The spike can also be reduced (but not eliminated) by thoroughly washing or vacuum treating the FeS_2 to remove acid-soluble impurities and elemental sulfur.

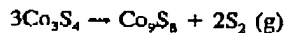
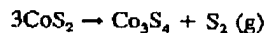
The Li/ FeS_2 electrochemical system has a number of important advantages over other systems, including Ca/CaCrO₄. These advantages include:

- Tolerance of a wide range of discharge conditions, from open circuit to high current densities
- High current capabilities; 3 to 5 times that of Ca/CaCrO₄
- Highly predictable performance
- Simplicity of construction
- Tolerance to processing variations
- Stability in extreme dynamic environments

As a result of these advantages, this system has become the predominant choice for a wide range of high-reliability military and space applications.

21.3.2 Lithium/Cobalt Disulfide

As a cathode vs. lithium in molten salt electrolyte cells, cobalt disulfide exhibits a slightly lower voltage than does iron disulfide. Cobalt disulfide has a greater thermal stability with respect to loss of sulfur, however. The decomposition reactions for cobalt disulfide at elevated temperatures are:



For iron disulfide at elevated temperatures:



Age s	Specific energy (Wh/kg)	Energy density (Wh/L)
	2.3	4.3
	1.3	5.0
2	1.0	3.5
15	0.4	2.1
	0.2	0.7
	2.8	6.8
	4.6	13.4
	3.8	11.1
	11.4	39.0
	26.2	82.0
	32.2	84.1
	33.1	77.0
	43.0	116.0
	38.7	111.8
	35.1	97.5

LiAl alloy, and Li metal. With the difference that s molten in an activated y be used with the same the basic LiCl-KCl euvity, or a lower-melting. Since the FeS_2 is a good prevent direct anode-to-lyte between the anode sc of a chemically com- is application."
stem because it does not rge depends on the type charge path for cathodes

second cathode transitions

1. For LiAl:

on)

CHAPTER 41

LITHIUM/IRON SULFIDE BATTERIES*

Gary L. Henriksen and Andrew N. Jansen

41.1 GENERAL CHARACTERISTICS

Investigations of electrochemical cells having alkali-metal electrodes and molten-salt electrolytes began in 1961 at Argonne National Laboratory (ANL) in an effort to develop thermally regenerative galvanic cells for the direct conversion of heat to electricity.¹ This work led to the invention of the lithium/sulfur cell in 1968, in which elemental lithium and sulfur were used as the active materials in the electrodes with molten LiCl-KCl electrolyte.² The melting point of the LiCl-KCl eutectic electrolyte is 352°C, which requires that the cell operating temperature be maintained above 400°C. Lithium and sulfur are attractive materials for a high-performance battery because they possess low equivalent weights, develop a high voltage (approximately 2.3 V), and are capable of high current densities (>1 A/cm²). Attempts to develop the lithium/sulfur cell were abandoned in 1973 because of problems in containing the active materials of both electrodes.³ These problems were overcome by substituting alloys of lithium for elemental lithium in the negative electrode and metal sulfides for elemental sulfur in the positive electrode.⁴

Lithium alloy/metal sulfide batteries employ a molten-salt electrolyte and solid porous electrodes. Depending on electrolyte composition, they operate over a temperature range of 375 to 500°C. Operation at these temperatures with molten-salt electrolytes achieves high power densities, due to the high electrolyte conductivities and fast electrode kinetics. A shift from prismatic battery designs to bipolar designs enhances the power characteristics further by reducing the battery impedance.

Alloys of lithium with aluminum or silicon are typically used as reversible solid negative electrodes. These alloys reduce the lithium activity—below that of lithium metal—to a controllable level, yielding high coulombic efficiencies. Development of a two-component lithium alloy ($\alpha + \beta$ Li-Al and Li₃Al₂Fe₂) negative electrode material provides an in situ overcharge tolerance capability by increasing the lithium activity in the negative electrode at the

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end of charge. This initiates a high-rate self-discharge reaction that allows continued passage of charging current—at or below the self-discharge rate—without further charge acceptance.⁵ Development of this in situ overcharge tolerance capability has rendered the bipolar design a viable option for lithium/iron sulfide batteries.

Several metal sulfides—iron, nickel, cobalt, and so on—can be used as positive electrodes. These metal sulfides relieve the vapor pressure and corrosion issues associated with the use of sulfur. Cost considerations lead to the selection of FeS or FeS₂ for commercial applications, while other metal sulfides remain viable options for specialty battery applications where cost is less important. Combining the dense FeS₂ positive electrode, operating only on its upper voltage plateau, with the low-melting LiCl-LiBr-KBr electrolyte has achieved a stable, reversible, and high-performance lithium/iron disulfide cell technology.

Refinements in the composition of this low-melting electrolyte and development of stable chalcogenide ceramic/sealants have led to the development of sealed electrolyte-starved bipolar Li/FeS and Li/FeS₂ cells and stacks.⁶ These cells and stacks exhibit high power and energy densities. As a result of the advances that have been made in high-performance bipolar cell and stack technology, it has replaced the prismatic design. In addition to its higher performance, the bipolar design is likely to be more cost-effective than the prismatic design, because it significantly reduces the quantity of nonactive materials used in the battery stack and thermal enclosure. The major advantages and disadvantages of bipolar lithium/iron sulfide batteries are summarized in Table 41.1. In addition to their high power and energy densities, they are tolerant to most types of abuse encountered in electric-vehicle applications. Due to their low internal impedances and favorable electrode kinetics, both ampere-hour and watt-hour capacities of these bipolar batteries are relatively independent of load. Also, they possess characteristics that render them inherently safe and reliable,⁷ whereas many other technologies have to engineer safety and reliability into their systems. Because it is a high-temperature battery, it is housed within a thermal enclosure and, therefore, is independent of environmental conditions. Its major disadvantages are those associated with high-temperature batteries—mainly the need for a thermal management system to maintain its temperature within acceptable limits and the need to consume stored energy to keep the battery hot during extended stand periods in locations where a source of external electric power is not available.

TABLE 41.1 Major Advantages and Disadvantages of Bipolar Lithium/Iron Sulfide Cells and Batteries

Advantages	Disadvantages
Combines high power and energy densities	Requires thermal management system to maintain operating temperature within acceptable window
Tolerant to overcharge, overdischarge, and freeze-thaw abuse	Consumption of stored energy may be required to maintain temperature, during extended stand periods
Capacity independent of load	
Inherently safe and reliable	
Independent of environmental conditions	

The main interest in high temperature batteries such as lithium/iron sulfide, sodium/sulfur, and sodium/nickel chloride is for electric vehicle applications due to their high specific power and energy possibilities. The replacement of the liquid lithium electrode with a solid LiAl alloy alleviated many of the safety concerns that plagued the other two systems, which are based on a liquid sodium electrode. In 1991, the United States Advanced Battery

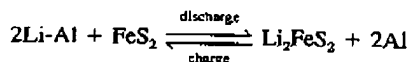
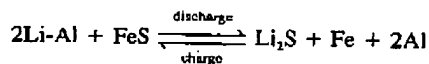
a long-term battery technology for electric vehicles. Although significant advances were made in this technology⁸ at the end of 1995, it was decided to discontinue R and D efforts in this technology in favor of the rapidly developing lithium-ion and lithium-polymer battery technologies. These newer technologies were also considered to be long-term developments by the USABC with power and energy capabilities similar to that of the LiAl/FeS₂ battery but which operate at much lower temperatures. Should interest revive in stationary energy storage (SES) batteries, lithium/iron sulfide batteries remain viable candidates for this application. The primary version of the lithium/iron sulfide battery continues to find wide usage as thermal batteries (see Chap. 21).

Development of the rechargeable lithium/iron sulfide battery is still continuing but no longer with molten salt electrolytes. The most notable work^{9,10} involves the replacement of the molten salt electrolyte and magnesia separator with a composite polymer electrolyte that operates at temperatures of 90 to 135°C. There are many advantages to operating this system at this reduced temperature range. This lower temperature permits the use of lithium foil instead of cold-pressed pellets of lithium-aluminum alloy. The positive electrode also does not need to be a cold-pressed pellet; it can be cast from slurry as is common for lithium-polymer and lithium-ion technologies. Steel and polymer seals can be used for the cell hardware instead of the molybdenum and ceramic seals required for high-temperature molten-salt batteries. This new direction for the lithium/iron sulfide battery looks promising and will hopefully result in a commercial battery. Although there are many similarities between the two technologies, the majority of the information presented in this chapter is based on the molten salt battery technology that was under development for nearly three decades.

41.2 DESCRIPTION OF ELECTROCHEMICAL SYSTEM

Secondary Li/Fe₂S₃ cells that were developed for electric-vehicle applications at ANL, incorporate cold-pressed FeS or dense FeS₂ positive-electrode pellets, two-component Li-Al/Li₂Al₂Fe₂ negative-electrode pellets, and LiCl-rich LiCl-LiBr-KBr/MgO electrolyte/separator pellets. Electrolyte of the same composition is incorporated in the positive- and negative-electrode pellets. The LiCl-rich electrolyte (34 mol % LiCl-32.5 mol % LiBr-33.5 mol % KBr) possesses a low melting point, broad liquidus region, and high conductivity.⁵ The high conductivity yields low area-specific impedance (ASI) from low-burdened electrolyte-starved cells. Li/FeS₂ cells employing this electrolyte can operate in the 400 to 425°C temperature range, compared with operation in the 450 to 475°C range for cells employing LiCl-KCl electrolyte. Use of this electrolyte with a dense FeS₂ positive electrode, which operates only on the upper voltage plateau (U.P.), has extended the cycle life for the Li/FeS₂ technology to more than 1000 cycles in flooded cells.¹¹ Comparable cycle life was demonstrated previously for the Li/FeS chemistry operating with LiCl-KCl electrolyte.¹²

The overall electrochemical reactions for the Li/FeS and U.P. Li/FeS₂ cells are



The theoretical specific energies for these two reactions are approximately 460 and 490 Wh/kg, respectively. The corresponding voltages for these reactions are approximately 1.33 and 1.73 V, respectively. The reactions are more complex than shown and involve the formation of intermediate compounds.^{9,10,13-17}

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41.3 CONSTRUCTION

The original hardware development programs used prismatic cell designs (Fig. 41.1) similar to those employed in most automotive SLI lead-acid batteries. Several flat-plate positive and negative electrodes are positioned vertically and separated by porous separator sheets to form a multiplate cell with the desired combination of ampere-hour capacity (for energy) and electrode surface area (for power). Historically BN (Boron Nitride) cloth or felt has been used as the separator in flooded-electrolyte cells, while MgO pressed-powder plaques have been used in starved-electrolyte cells. Perforated metal sheets are positioned between separators and electrodes to restrain the movement of particulate matter from the electrodes into the separator. Photoetching is used to perforate the metal sheets. Steel is used as the current collector for FeS positive electrodes, while molybdenum is the most commonly used current collector for FeS₂ positive electrodes. In these prismatic cells the negative electrodes are typically grounded to the cell case, while the positive electrodes are connected to a feed-through terminal that is electrically insulated from the cell case. In many designs "picture-frame" structures are used to locate and hold together electrode components as a unit.

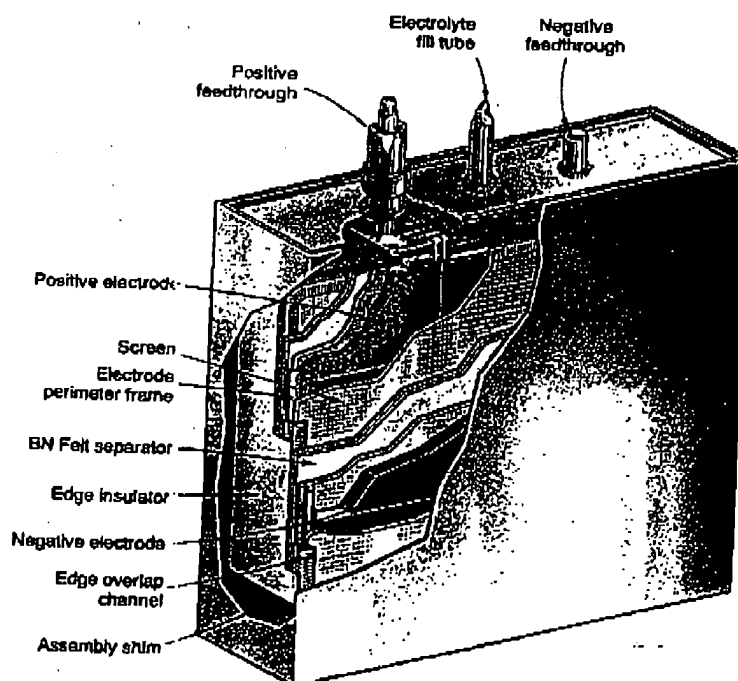


FIGURE 41.1 Cutaway view of flooded prismatic Li-Al/FeS cell showing arrangement of electrodes, separators, and internal current-collector system. (Courtesy of Argonne National Laboratory.)

LITHIUM/IRON SULFIDE BATTERIES 41.5

Lithium/iron sulfide prismatic cells can be assembled in a charged, uncharged, or partially charged state. When assembled in the charged state, the negative electrodes are cold-pressed using a mixture of the two-component alloy, ($\alpha + \beta$) Li-Al and Al_3Fe_2 , and electrolyte powders. The positive electrodes are assembled in a similar manner, using a mixture of FeS_2 and electrolyte powders. When assembled in the uncharged state, the FeS positive-electrode plaque is pressed using an appropriate mixture of Li_2S , Fe, and electrolyte powders, while the FeS_2 positive-electrode plaque is formed using a mixture of LiFeS_2 and electrolyte powders. The negative-electrode plaque is pressed using an appropriate mixture of $\alpha\text{-Al}$, Al_3Fe_2 , and electrolyte powders. Partially charged cells can be assembled using appropriate mixtures of the charged and uncharged starting materials.

As a result of several technical advances in the late 1980s and early 1990s (Table 41.2) the design of choice today is the bipolar stack (Fig. 41.2).^{4,15} Cell stacks are formed by placing positive-electrode, electrolyte/separator, and negative-electrode pressed-powder plaques into a prefired seal-ring assembly and performing a final weld on the metal bipolar plate (current collector/cell wall) of one cell to a metal ring buried in the seal-ring assembly of an adjacent cell. In a manner similar to the prismatic design, particle retainer screens can be positioned between the electrode and the separator/electrolyte plaques. In an effort to minimize weight and volume, bipolar cells and stacks employ MgO separators in an electrolyte-starved configuration. Also, cells employing overcharge-tolerant two-component lithium alloy negative electrodes require the use of separators made of MgO, or other electrically insulating materials that are stable to the higher lithium activity associated with the overcharge alloy. As described for the prismatic cells, bipolar cells can be assembled in the charged, uncharged, or partially charged state.

The key to designing and constructing practical bipolar stacks is the development of a suitable seal material for making metal-to-ceramic peripheral seals. This was accomplished in 1990 with the development of chemically stable chalcogenide sealants that bond tenaciously to both metals and ceramics.¹⁶ These sealants can be specially formulated to accommodate differences in thermal expansion between metals and ceramics by forming graded seals. They exhibit more than 95% coverage and wetting angles approaching 0° for both steel and molybdenum. Compared to commercially available high-temperature bonding agents, the standard chalcogenide sealant materials exhibit bond strengths which are an order of magnitude greater.^{17,18}

TABLE 41.2 Major Technical Advances in Development of Bipolar Li-Al/ FeS_2 Cells

Time frame, year	Major technical advance	Practical implication
1986	Low-temperature electrolyte and upper-plateau dense FeS_2 cathode	Achieves > 1000 cycles
1988	Electrochemical overcharge tolerance	Makes bipolar design variable
1989	Lithium-rich electrolyte in starved cell	Enhances performance
1990	Chalcogenide seal material	Makes bipolar design practical

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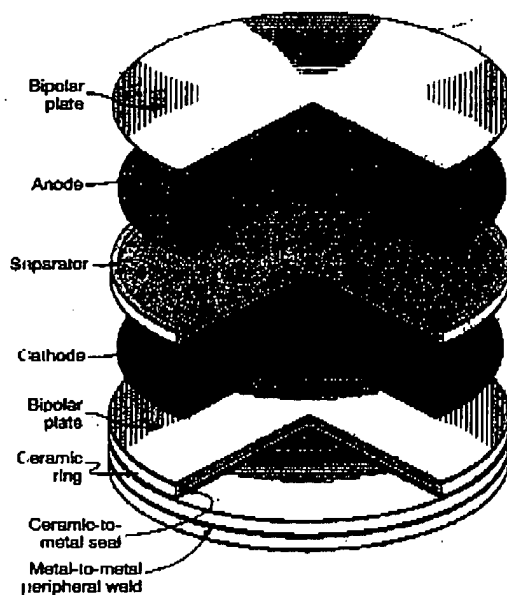


FIGURE 41.2 Exploded view of four-cell bipolar Li-Al/FeS₂ stack under development for electric-vehicle applications shown electrodes, separator, and bipolar plate current collector. (Courtesy of Argonne National Laboratory.)

41.4 PERFORMANCE CHARACTERISTICS

41.4.1 Voltage

The open-circuit voltage of the Li-Al/LiCl-LiBr-KBr/FeS cell is 1.33 V at 425°C, while that of the Li-Al/LiCl-LiBr-KBr/FeS₂ (U.P.) cell is 1.73 V.^{6,15} The operating voltages of these cells are in the ranges of 0.9 to 1.3 V for the Li-Al/FeS cell and 1.2 to 1.7 V for the Li-Al/FeS₂ U.P. cell. Charge voltage cutoffs are approximately 1.6 and 2.0 V, respectively. Charging at these voltages can be conducted for extended durations due to the overcharge tolerance capability provided by the two-component lithium alloy negative electrode.¹⁷

41.4.2 Discharge Characteristics

A typical set of cell voltage versus delivered ampere-hour capacity discharge curves for 13-cm-diameter bipolar U.P. Li-Al/FeS₂ and Li-Al/FeS cells is given in Fig. 41.3.¹⁷ The step in both discharge curves, occurring at 5 to 7 Ah into the discharge, is associated with the transition from the overcharge-tolerant negative-electrode alloy phase to the normal $\alpha + \beta$ Li-Al alloy negative-electrode phase. Both types of cells exhibit good voltage stability throughout the discharge.

The effect of discharge rate on delivered capacity for both types of cells is illustrated in Figs. 41.4 and 41.5 for two 3-cm-diameter cells. The reduction in capacity associated with increasing the discharge rate is less for these technologies than it is for most other battery

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The prismatic Li-Al/FeS batteries, previously under development for electric-van applications, are projected to meet the light-duty van requirements and those of slightly more demanding electric-vehicle applications. Bipolar Li-Al/FeS batteries are projected to meet or surpass the performance requirements of most electric-vehicle applications, including the very demanding requirements of the high-performance passenger car. Bipolar Li-Al/FeS₂ batteries are projected to surpass the requirements of all three vehicle batteries, including the extremely demanding requirements of the hybrid-vehicle battery. The modeling results indicate that a bipolar Li-Al/FeS₂ battery, designed to fit the space available in the Impact, could deliver 40 kWh of energy, which corresponds to an estimated 560 km zero-emissions range. Also, at the power-to-energy ratio of 2, this battery technology is projected to approach the long-term performance objective of the USABC. Examples of battery design summary information for electric and hybrid vehicles are provided in Table 41.8. The information contained in this table indicates the high degree of packaging flexibility associated with this battery technology. For example, the three hybrid-vehicle battery designs vary rather dramatically in shape, while retaining high volumetric and gravimetric power and energy densities.

TABLE 41.8 Selected Summary Information from Computer-Aided Battery Design Model Used in Projecting Battery Performances

Battery designation	High-Performance electric vehicle			Hybrid vehicle		
	EV-1	EV-2	EV-3	Hybrid-1	Hybrid-2	Hybrid-3
Power, Kw	90.0	90.0	90.0	90.0	90.0	90.0
Energy store, kWh	40.0	40.0	40.0	18.0	15.0	15.0
Number of parallel strings	2	3	3	2	2	3
Shape of battery cross section	Oval	Triangle	Triangle	Oval	Rect.	Rect.
Stacks per cross section	2	3	3	2	4	6
Total number of stacks	6	6	6	6	4	6
Total number of cells	378	570	570	378	380	570
Cell parameters:						
Cell diameter, cm	16.1	13.4	13.4	16.1	16.3	13.4
Cell thickness, cm	1.126	1.108	1.025	0.587	0.505	0.424
Separator thickness, mm	1.2	1.2	0.5	1.2	1.2	0.5
Welding ring type	Channel	Channel	Channel	Flat	Flat	Flat
Battery performance summary						
Battery dimensions:						
Height, cm	36.8	29.5	29.5	36.8	37.1	31.4
Width, cm	20.4	31.4	31.4	20.4	37.1	45.0
Length, cm	232.0	226.8	211.1	130.1	31.4	53.6
Battery volume, L	155.9	158.6	147.6	87.4	79.6	72.9
Battery weight, kg	282.4	281.5	265.2	161.3	137.0	125.2
Specific power:						
Per unit volume, W/L	577.3	567.5	609.7	1030.0	1130.4	1234.2
Per unit weight, W/kg	318.7	319.7	339.4	558.0	657.0	718.7
Specific energy:						
Per unit volume, Wh/L	256.6	252.2	271.0	206.0	188.4	205.7
Per unit weight, Wh/kg	141.6	142.1	150.8	111.6	109.5	119.8

LITHIUM/IRON SULFIDE BATTERIES 41.21

An artist's rendering of a full-size 50-kWh van battery, using prismatic Li-Al/FeS cells, is shown in Fig. 41.16. These multiplate prismatic cells contain the full ampere-hour capacity required for the van application and are all series-connected electrically to provide the desired voltage. As illustrated, metal intercell connectors are used to connect adjacent cells electrically, one to the other. A double-walled steel vacuum jacket, filled with compressed multifoil insulation, provides thermal insulation for the battery. A forced-air heat exchanger is located inside the thermal enclosure in direct contact with the cells. This heat exchanger is used to prevent overheating during high-power operation. Resistance heaters (not shown) are provided inside the thermal enclosure for heating the battery to operating temperature and providing supplemental heat during extended stand periods. All leads from inside the battery are brought through a thermally insulated end cap or cover.

For bipolar lithium/iron sulfide electric-vehicle batteries, the packaging flexibility is significantly enhanced. An artist's concept of a self-contained thermally insulated 114-V 5-kWh bipolar battery module is provided in Fig. 41.17. The compactness and the cylindrical shape of bipolar stacks allow consideration of small self-contained modules that utilize lightweight loosely wrapped multifoil insulating jackets, of the type shown.²³ The walls of these small cylindrical insulating jackets are sufficiently strong to negate the need for compressed multifoil insulation layers between the walls to provide structural support. These lightweight jackets exhibit excellent insulating properties when under vacuum. Also, a simple concept is shown for altering the pressure between the walls of the jacket by controlling the temperature of a chemical getter material.²⁵ By heating the getter, the gas pressure between the jacket walls can be raised to permit a higher rate of heat rejection through the jacket for the purpose of cooling the battery without a forced-air heat exchanger. Use of these small self-contained thermally insulated modules does not significantly increase the weight and volume burden associated with the thermal enclosure over the type described for prismatic batteries, yet they appear to offer significant advantages from the standpoint of packaging the battery in the vehicle. Although detailed reliability and safety studies have not yet been performed on bipolar lithium/iron sulfide batteries, they possess favorable inherent characteristics in both areas. In the reliability area, cells routinely develop low-resistance internal short circuits when they reach the end of life. This characteristic permits bipolar stacks—employing strings of series-connected cells—to remain operational following the loss of one or more cells. The loss of energy for the stack is essentially limited to the energy content of the failed cell or cells. Therefore complex cell interconnect schemes, or other methods of making battery reliability and life less sensitive to cell failure, are not needed for lithium/iron sulfide batteries.

In the safety area, the active materials (lithium alloy anodes and FeS₂ cathodes) are solids at both room temperature and operating temperature. Once the battery is heated to operating temperature, the molten-salt electrolyte provides a protective coating over the active materials. Even in the case of a very severe accident, where the battery enclosure and cell walls are breached, this electrolyte coating provides protection against the direct exposure of ambient air to the active materials. This was demonstrated in tower drop tests, where the cases of prismatic Li-Al/FeS cells—preheated to operating temperature—ruptured upon impact.¹⁹ The contents of these cells were spewn on the ground, but no combustion of active materials or release of toxic fumes occurred. Other factors concerning safety, such as chemical, thermal, and electrical hazards (short circuit, overdischarge, and overcharge) have been examined. While extensive safety tests have not been conducted on battery systems, those that have reaffirm the development experience which indicates that these batteries are inherently quite safe.⁷

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cations more
likely to meet
the requirements
of the Li-Al/FeS₂
cells, including
the results of
impact, emissions
approach
summary
formation
with this
other dra-
gery den-

Used in

Hybrid-3

90.0

15.0

3

Rect.

6

6

570

13.4

0.424

0.5

Flat

31.4

45.0

53.6

72.9

125.2

1234.2

718.7

205.7

119.8

41.22 CHAPTER FORTY-ONE

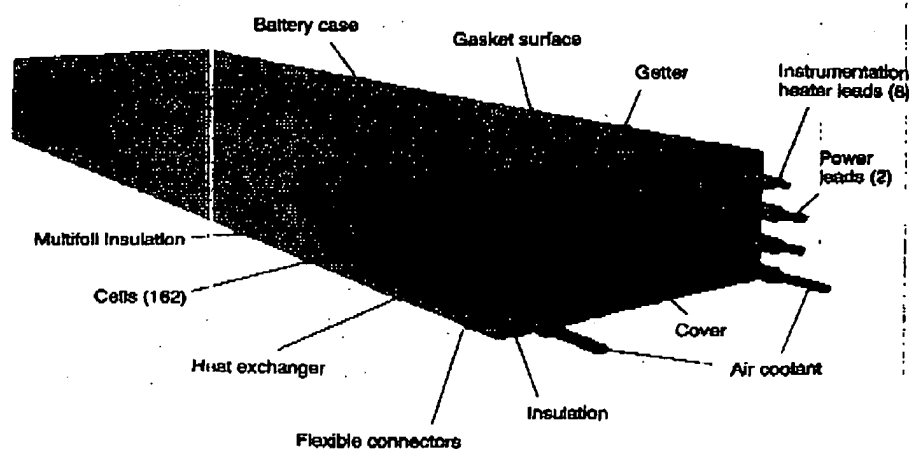


FIGURE 41.16 Artist's concept of full-scale Li-Al/FeS electric van battery with cutaway showing prismatic cells, heat exchanger, and compressed multifoil insulation. (From Chilenskas et al.,¹⁴ Courtesy of Argonne National Laboratory, University of Chicago.)

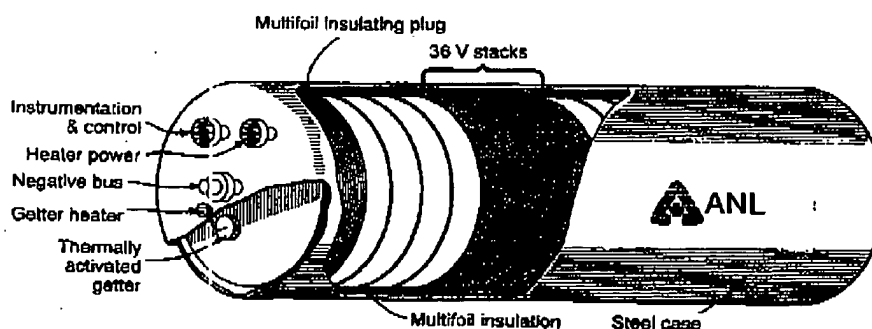


FIGURE 41.17 Artist's concept of thermally insulated electric-vehicle battery module with cutaway showing bipolar Li-Al/FeS stack, lightweight loosely wrapped multifoil insulation, and thermally activated getter system for controlling heat transfer from module. (Courtesy of Argonne National Laboratory.)

REFERENCES

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3. D. R. Vissers, Z. Tomczuk, and R. K. Steunenberg, "A Preliminary Investigation of High Temperature Lithium/Iron Sulfide Secondary Cells," *J. of the Electrochemical Society*, Vol. 121, 1974, p. 665.